# Influence of Confinement on Dynamical Heterogeneities in Dense Colloidal Samples

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# The Foundation

Adam & Gibbs Hypothesis:

Flow in a super-cooled liquid involves the cooperative motion of molecules. The structural arrest at glass transition is due to a divergence of the size of cooperatively rearranging regions.

P.N. Pusey & W. van Megen (Nature 320,340 1986)

Studied the effect of increasing particle concentration of colloidal fluids. They observed that it is possible to have concentrations that do not crystallize but behave as a "colloidal glass".

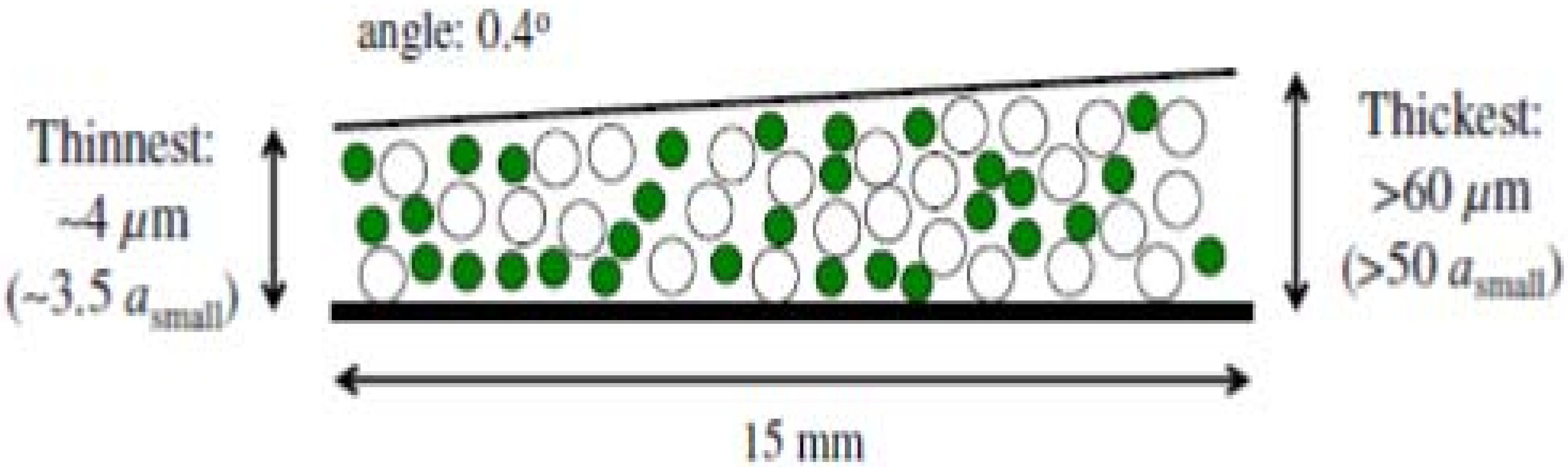
The idea:

Use dense colloidal suspensions to study molecular interactions of glass forming liquids.

# The Details

- Used spherical particles of two different radii (1.18 & 1.55 micrometers) to prevent crystallization Small/Large=3.5
- Sterically-stabilized to prevent inter-particle interaction and suspended in two solvents that matched their density.
- Used high speed confocal microscopy to rapidly visualize and acquire 3D images of particle positions.
- Used a wedge shape to study a range of confinement thickness that is "thin film like".

# To Help Visualize



# More Background

- Roel Dullens & Willem Kegel (2004).
  - Presence of wall induces a quasi-two dimensional ordering of dense colloidal suspension. The highly ordered yet not crystalline, quasi-2D layers along the walls serve as templates for subsequent layering in the samples interior.
- Adam & Gibbs, J. Chem. Phys. 43, 139 (1965)
  - Cooperatively rearranging regions are a super-cooled liquid's means of increasing its configurational entropy.
- Cooperatively Rearranging Regions (conceptually)-
  - Groups of neighboring molecules that collectively rearrange their positions to realize a new position in space.

# Defining Cooperatively Rearranging Regions

3 Elements:

1. Time scale used to determine displacements.
2. Threshold for considering a displacement a "rearrangement".
3. Definition of which particles are adjacent such that their motion is "cooperative".

# Rearrangement threshold

Rearranging particles have displacements that are larger than normal and lie in the tails of distribution curve.

Rahman, Phys. Rev. 136, A405 (1964).

Importance of outliers is calculated using

$$\alpha_2(\Delta t) = \frac{\langle \Delta x^4 \rangle}{3\langle \Delta x^2 \rangle^2} - 1,$$

Mobility threshold separates "rearrangements" from "caged" displacement. (Top 10% of mobile particles.)

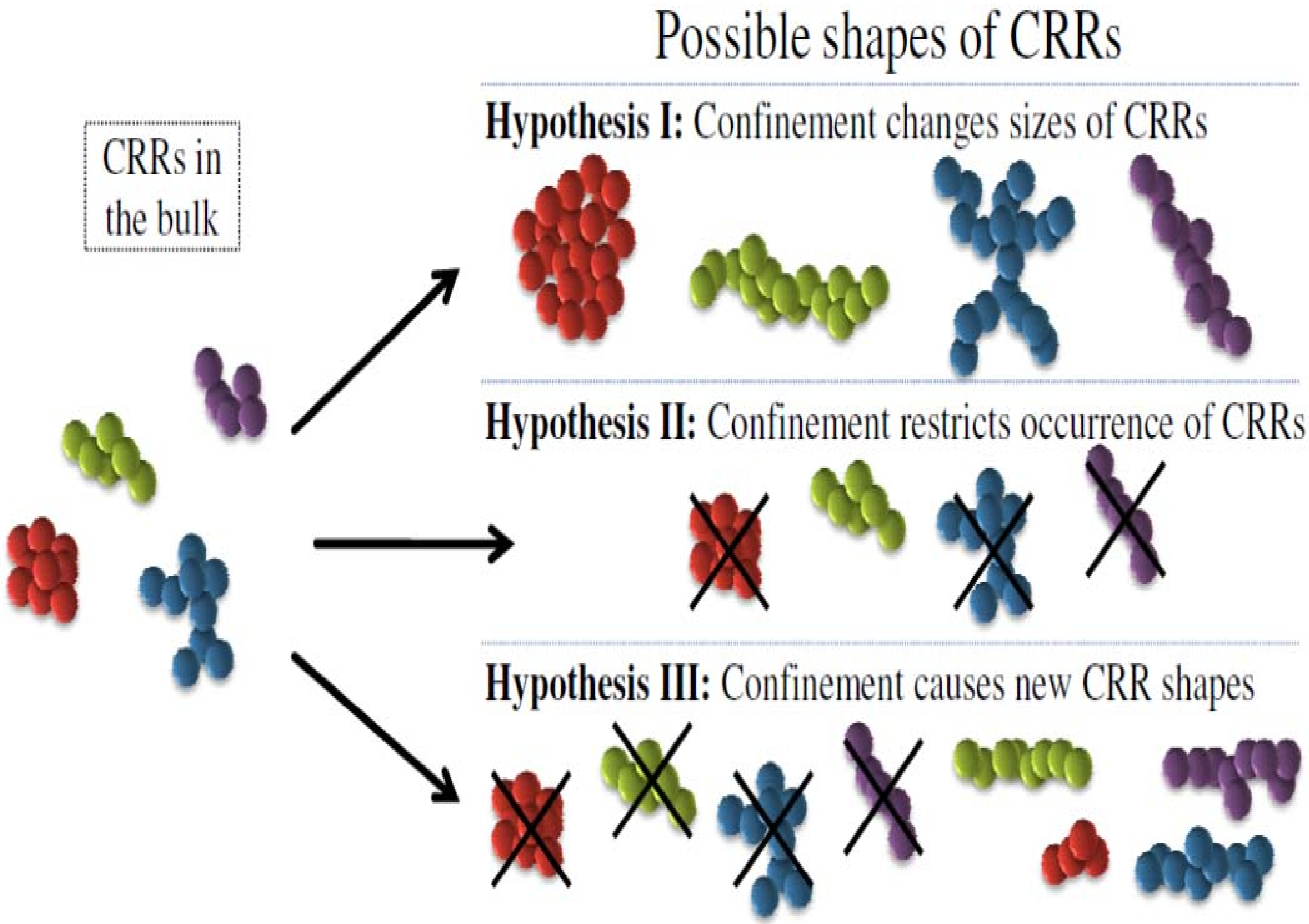
# In case you're skeptical

Lynch et al.

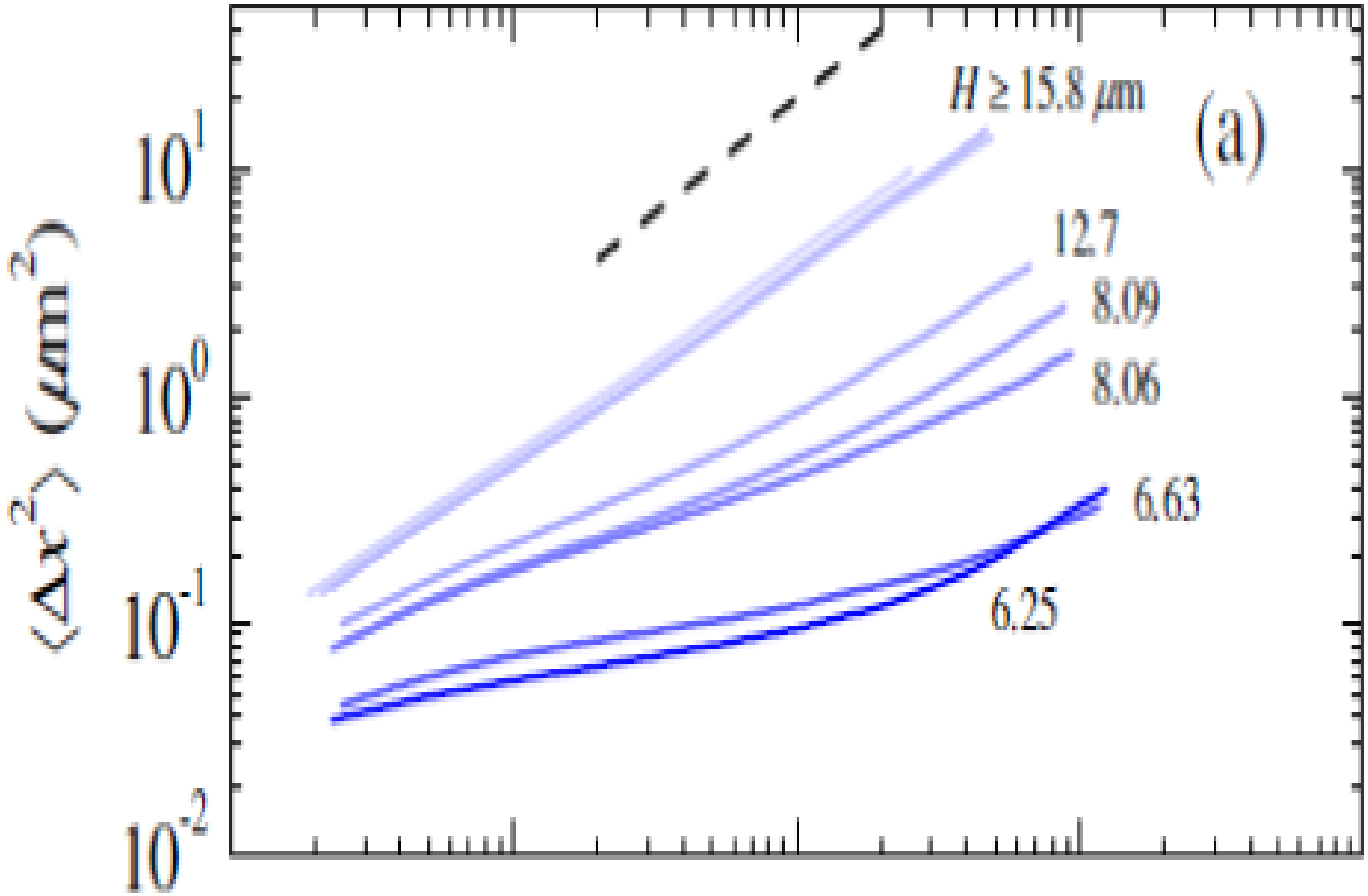
Showed cooperative dynamics of one species were often similar to that of the other.

Therefore the inability to observe larger particles does not prevent drawing conclusions regarding the role of cooperative behavior in confinement.

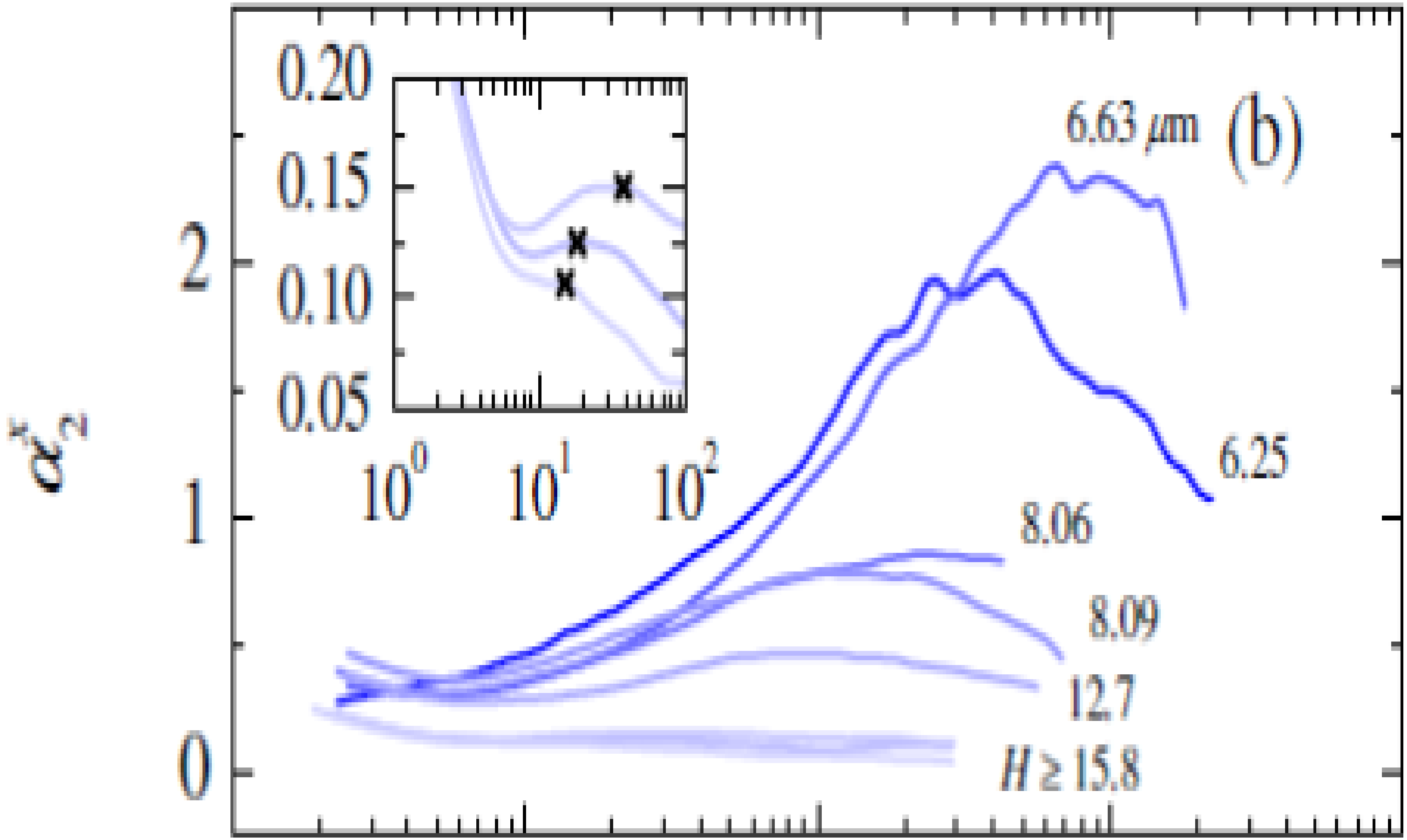
A CRR may be connected by unseen larger particle and this would limit apparent CRR sizes but not effect overall characteristics.


Possible shapes of CRRs
CRRs in the bulk
Hypothesis I: Confinement changes sizes of CRRs
Hypothesis II: Confinement restricts occurrence of CRRs
Hypothesis III: Confinement causes new CRR shapes

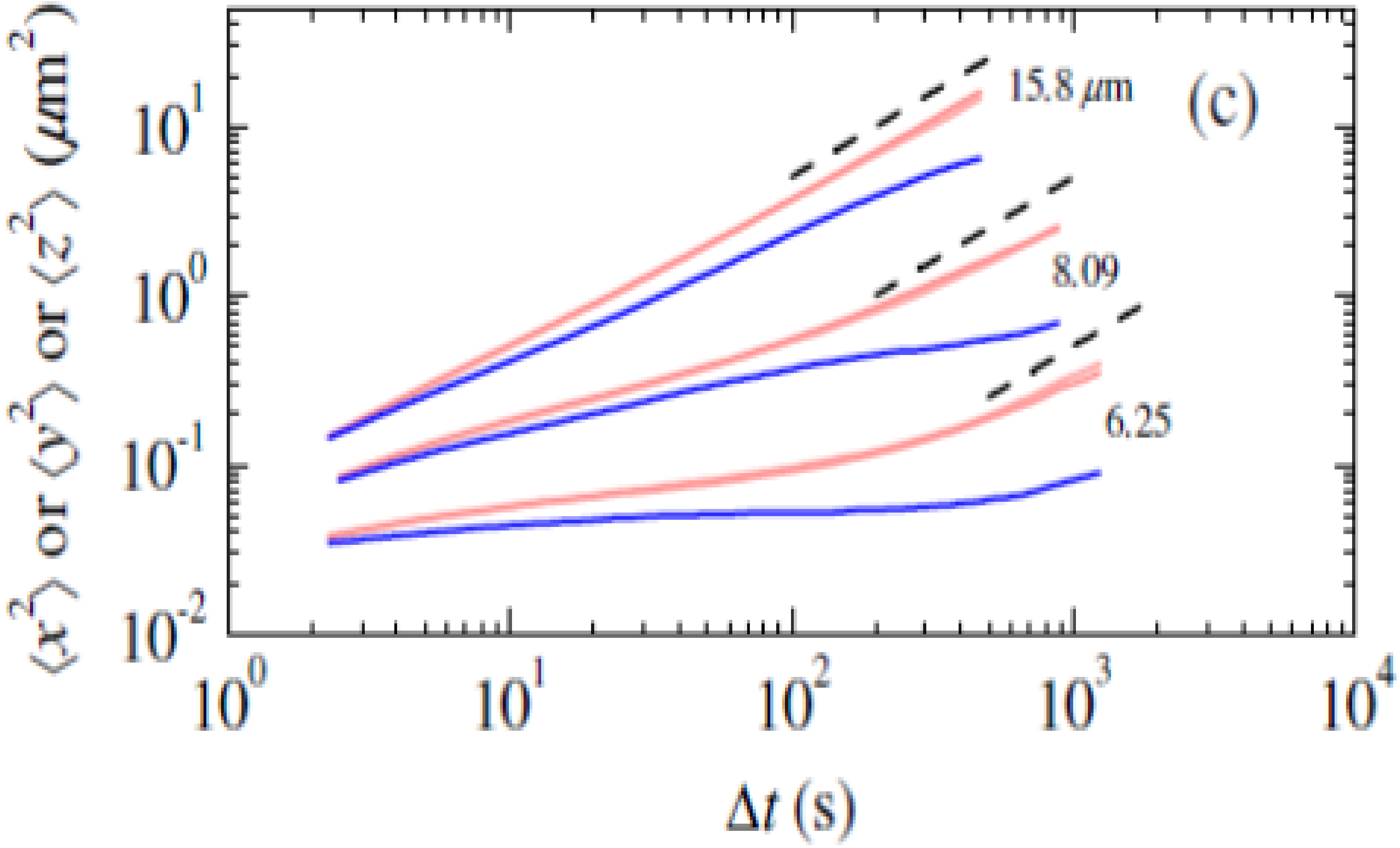
# Slowing dynamics: Average squared displacement v. Time



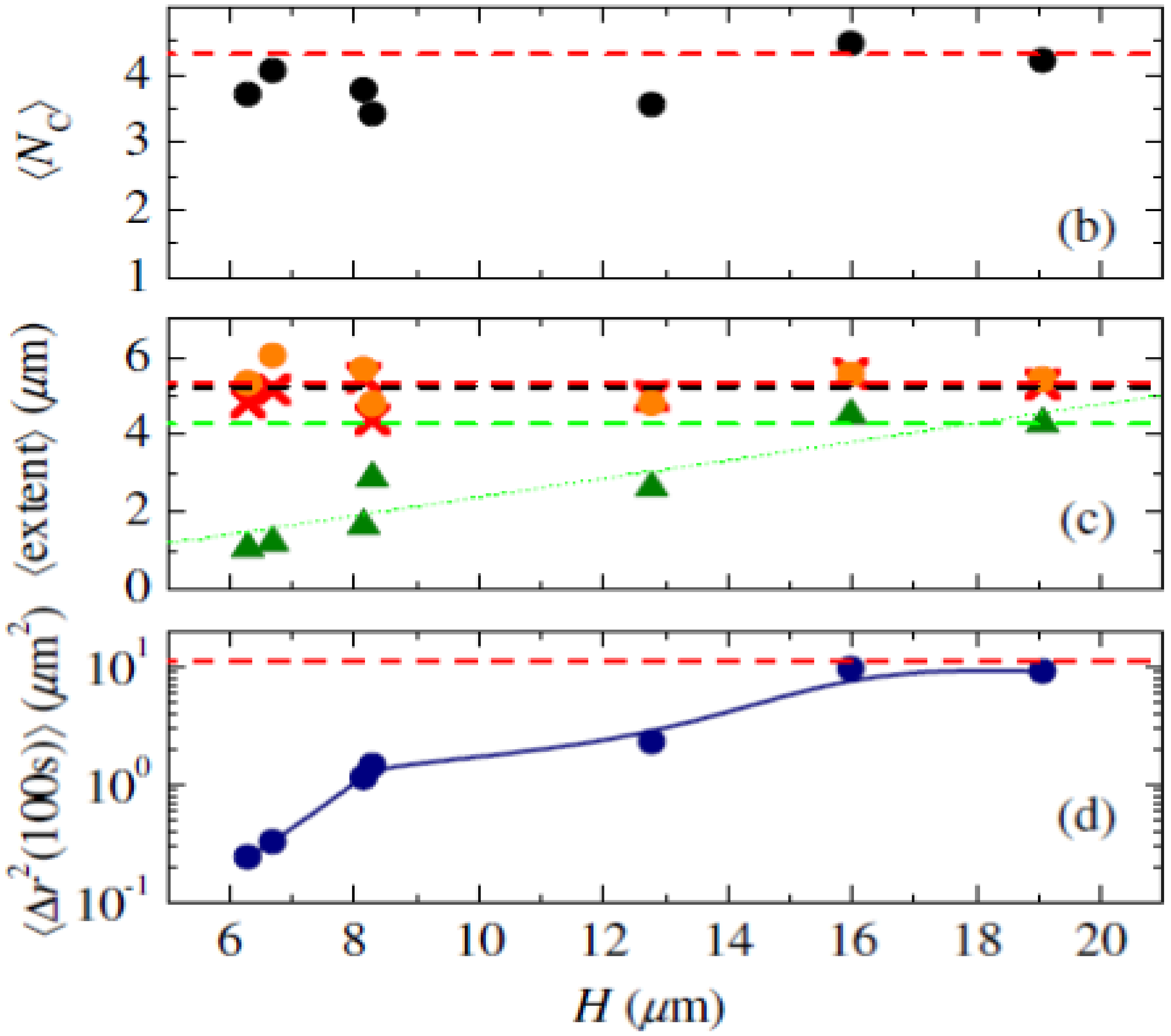
# Increasing Importance of Outliers with Decreasing H v. Time



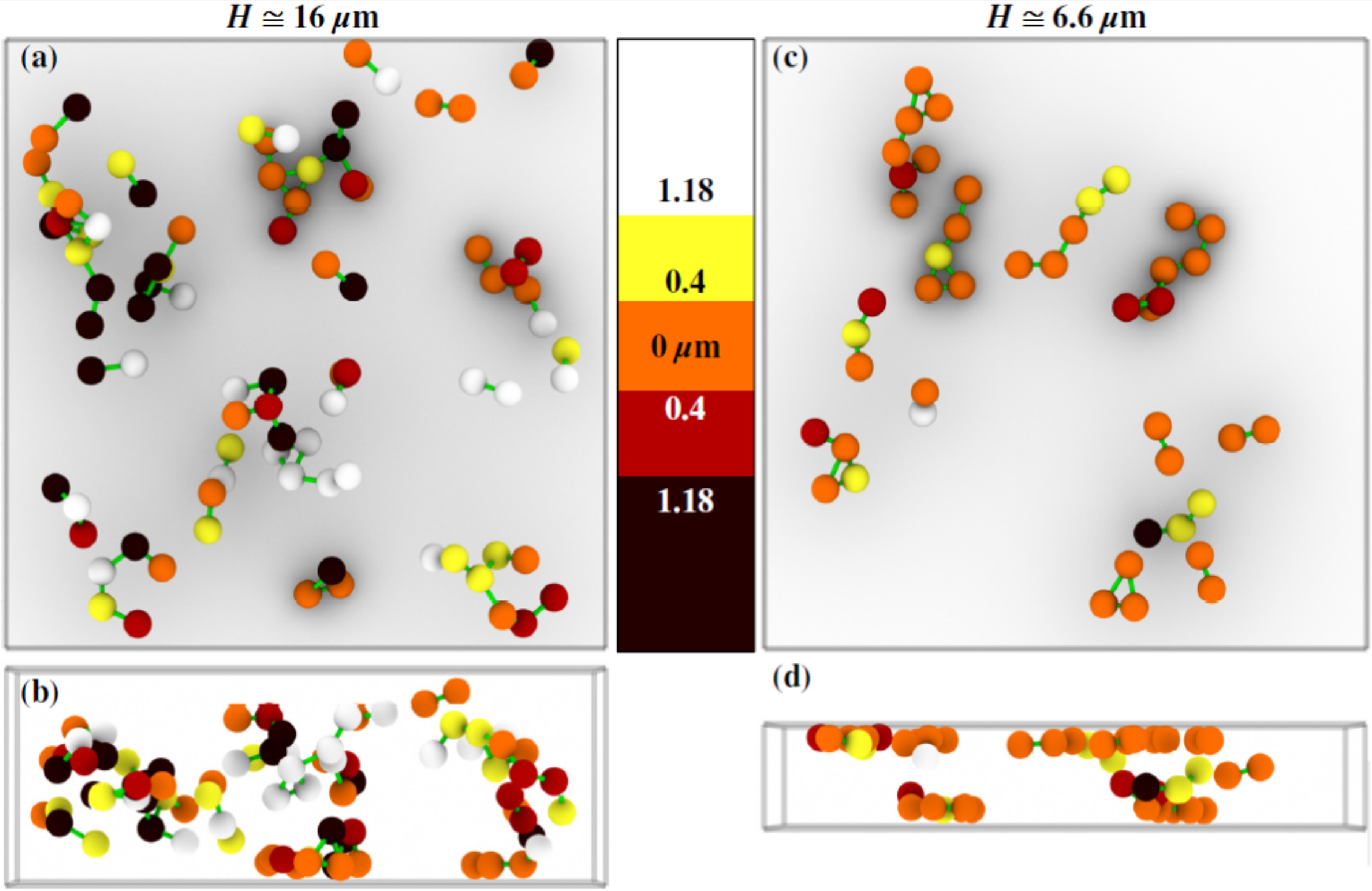
# MSD curves for all Directions: Showing Reduced Perpendicular Movement



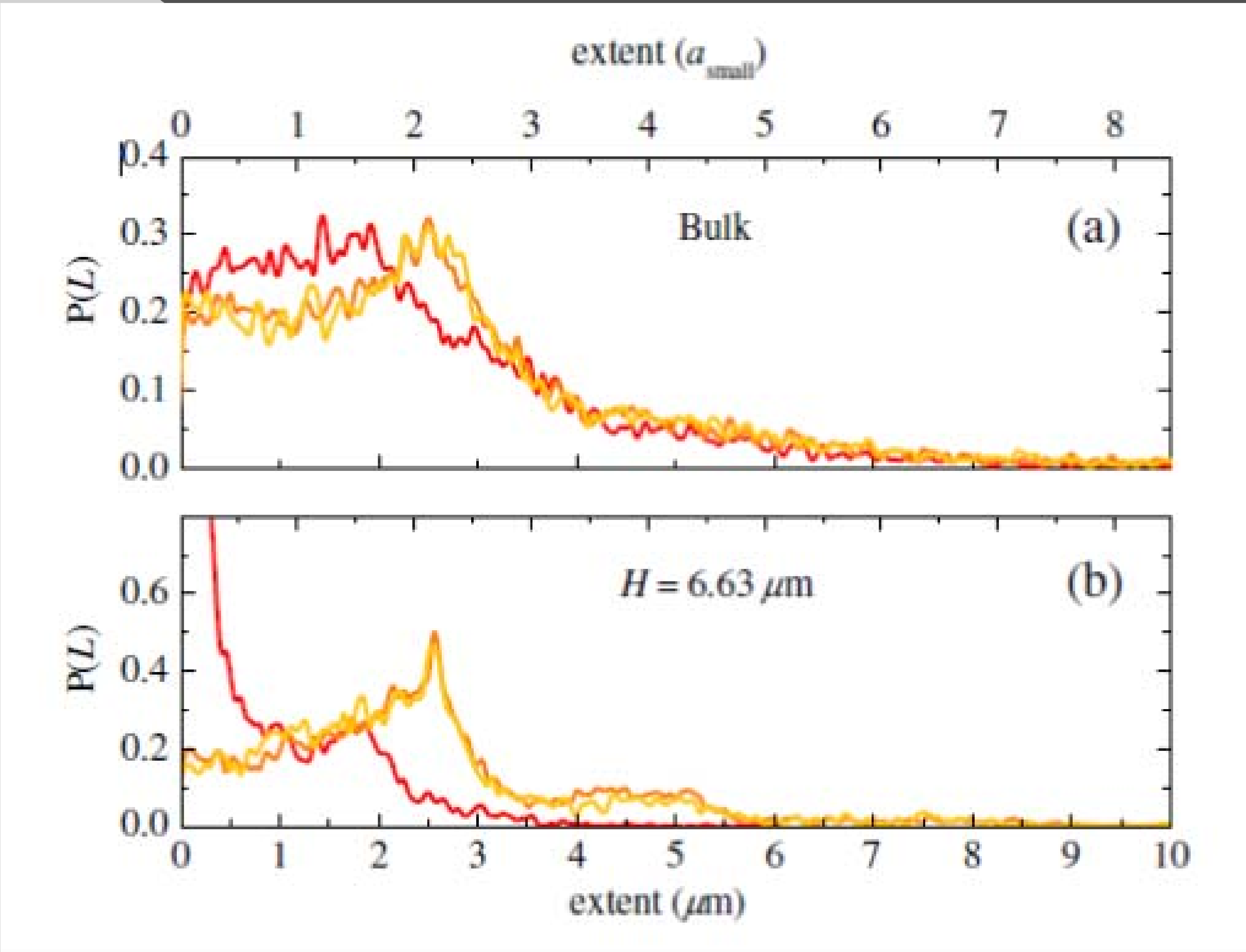
# Collective Cooperatively Rearranging Regions Data



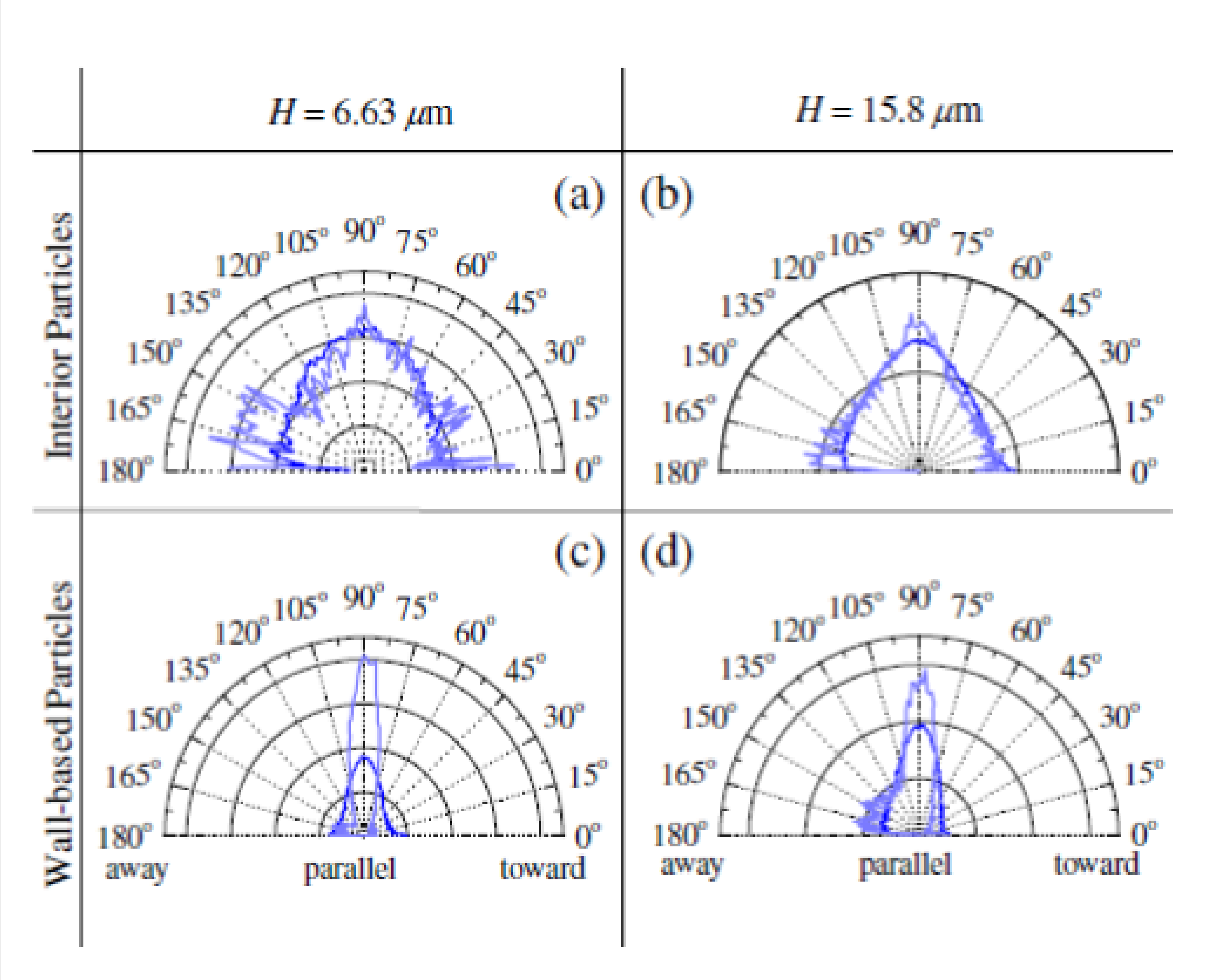
# Visual Graph to Show Shapes and Average Perpendicular movement



# Even More Analysis



# Probably a little over kill....



# Application

- The hope is that understanding the effects of confinement on the glass transition will help the understanding of the glass transition in general.
- More immediately, understanding the properties of confined fluids has direct relevance to lubrication and the flow of fluid through micro-fluidic devices.
- Possibly potential relevance to protein folding.

# To Σ it up

Thickness at which slowing is observed corresponds to confinement length-scale at which CRR become planar in shape.

Previous work by the same people shows thickness at which these regions begin to flatten will increase with higher volume fractions.

Next: How will the results change when walls have texture that frustrates the formation of layers. (As of now has only been studied in simulations.)